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Research Article

Studies on Inhibition of Mild Steel Corrosion by Copper (II) Complexes with some Amino Acids

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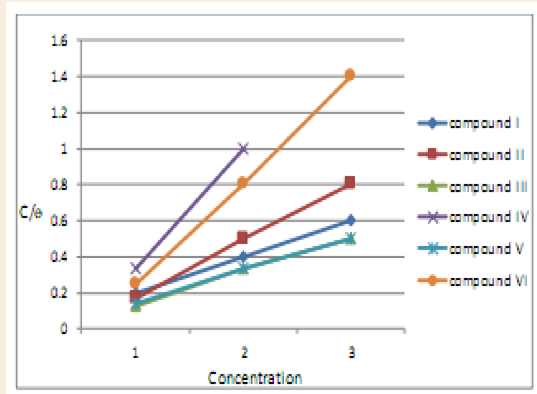
Abstract

The inhibition on mild steel corrosion in 1 M HCl solution was studied by weight loss method at room temperature by use of copper(II)complexes containing aminoacids such as glutamine, cysteine and aspartic acid with pyridine or triphenylphosphine as inhibitors. All tested complexes showed inhibition effect against mild steel corrosion. [CuCl(SCys)PPh$_3$H$_2$O] complex was found to act as excellent corrosion inhibitor at 3 mmol concentration. From weight loss measurements it was revealed that the efficiency of corrosion inhibition increases with the increase of inhibitors concentration. The inhibition action of these complexes explained on the basis of adsorption on the metal surface according to Langmuir's adsorption isotherm model.



Keywords: Weight loss method, amino acids, corrosion inhibitor

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Introduction

Mild steel is extensively used important industrial material because of its excellent mechanical properties, easy availability and low cost. [1]. Steel has been known to exhibit industrial applications such as construction material for cooling tower reservoirs, storage tanks, reaction vessels, chemical batteries, steam generators and pipelines for petroleum industries[2,3]. Hydrochloric acid solutions are widely used for removing scales and rust from the boiler surface, pickling of steel, ore production, acid cleaning and oil well acidification [4].These process cause dissolution of metal or corrode steel surface due to the aggressive nature of the acid [5].

The use of chemical inhibitors is the most practical method to reduce corrosion of the metals in acid medium [6]. Most of the available effective inhibitors are organic compounds such as trizoles, tetrazoles and containing nitrogen, oxygen, and sulfur groups [7]. But most of these compounds are toxic, expensive and affect living organism and environment. It is needed to develop environmental friendly and non toxic alternative inhibitors [8]. It is reported in many literature that the amino acids are act as good inhibitor for corrosion of variety of metals. Considerable attention has been directed towards amino acid inhibitors because of its easy to produce with high purity at low cost, non toxic and soluble in aqueous media [9].

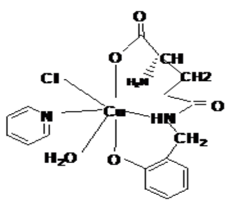
The aim of the present work is to synthesize copper complexes derived from aminoacids and investigate their corrosion inhibition efficiency towards mild steel by weight loss method. Amino acids glutamine, cysteine and aspartic acid are used in this work.

Experimental

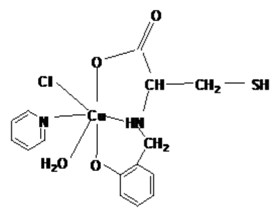
Synthesis of Cu(II) complexes

Amino acid (10 mmol) (glutamine or cysteine or aspartic acid) was dissolved in 10 mL distilled water with KOH (0.56 g, 10 mmol). Salicylaldehyde (1.22 g, 10 mmol) dissolved in 10 mL ethanol was added to amino acid solution and stirred for 3 h at RT. It was cooled in an ice path, reduced with 5 mL of sodiumborohydride (0.378 g, 10 mmol) containing few drops of NaOH solution. The pH of the solution was adjusted to 3.5 – 6 using few drops of con HCl to obtain the solid precipitate. The obtained aminoacid ligand wad washed and dried in RT. Copper chloride dihydrate (1.70 g, 10 mmol) was dissolved in 15 mL ethanol. Pyridine or triphenylphosphine (0.79g or 2.62 g, 10 mmol) was dissolved in 10 mL ethanol and transferred to copper chloride solution. It was stirred for 10 minutes. The corresponding aminoacid ligand (10 mmol) was dissolved in 10 mL distilled water with KOH (1 mL, 0.01M) was added to it and allowed to stir for 2h at room temperature. The reaction mass was filtered and allowed to evaporate at RT [10].

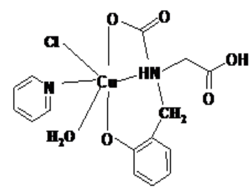
The copper amino acid complexes used as inhibitors in this study are given in **Figure 1**



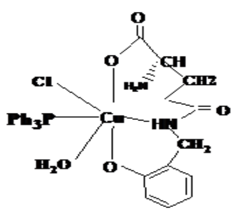
$[CuCl(SGln)pyH_2O]$
Compound I



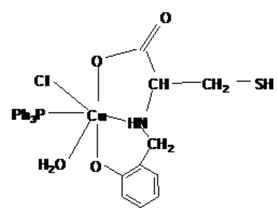
$[CuCl(SCys)pyH_2O]$
compound III



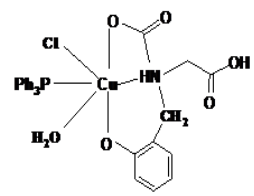
$[CuCl(SAsp)pyH_2O]$
compound V



$[CuCl(SGln)PPh_3.H_2O]$
Compound II



$[CuCl(SCys)PPh_3H_2O]$
compound IV



$[CuCl(SAsp)PPh_3H_2O]$
compound VI

Figure 1 Copper(II)aminoacid complexes used as inhibitors in this study

Weight loss measurements

A solution of 1M con.HCl used as corrosive medium was prepared by dilution of A.R grade acid using distilled water. Copper aminoacid complexes were made in to three different concentrations 1mmol, 2 mmol and 3 mmol. Mild steel coupons of dimension 4 cm × 1 cm × 0.1 cm were abraded with different emery papers, degreased by acetone, washed with distilled water and dried at RT. A small hole was made on upper edge of the coupon so that the coupon could be hanged in solution.

Results and Discussion

The corrosive medium 1 M HCl (100 mL) was taken in 250 mL glass beakers. The copper(II) aminoacid compounds I-VI with 1 mmol, 2 mmol and 3 mmol concentrations were added in the beakers and one beaker without inhibitor kept as control. The previously weighed specimens were immersed in hanging position in the experimental solution at RT. After three days, the specimens were removed, polished with emery papers, washed with distilled water degreased with acetone, dried and reweighed. The weight differences were measured and the efficiency of the inhibitor was calculated using the following equation

$$\text{Inhibition efficiency, \% IE} = \frac{W_0 - W_1}{W_0} \times 100 \quad \text{-----------------------------} \quad (1)$$

W_0 - weight loss in the absence of inhibitor and W_1 - weight loss in presence of inhibitor

The corrosion rate (in mpy-1 millimetre penetration per year) was expressed by the following equation

$$\text{Corrosion rate CR} = \frac{534\ W}{DAt} \quad \text{-----------------------------} \quad (2)$$

W - weight loss(g)
D - density of the specimen(7.85 g/cm^3)
A - surface area of specimen(cm^3)
t - immersion time(days)

The weight loss, the efficiency of inhibitors and corrosion rate are presented in **table1**.

Table 1 Percentage efficiency and corrosion rate of copper(II) aminoacid complexes

S.No	Name of the inhibitor	concentration	Control (W_0)	Weight loss (W_1)	% efficiency	Corrosion rate(mp/y)
1	Compound I	1 mmol	0.12	0.08	33.3	0.45
		2 mmol		0.05	583	0.28
		3 mmol		0.05	58.3	0.28
2	Compound II	1 mmol	0.12	0.06	50	0.34
		2 mmol		0.04	66.6	0.22
		3 mmol		0.04	66.6	0.22
3	Compound III	1 mmol	0.48	0.08	83.5	0.45
		2 mmol		0.06	87.5	0.34
		3 mmol		0.06	87.5	0.34
4	Compound IV	1 mmol	0.48	0.03	93.7	0.17
		2 mmol		0.02	95.8	0.11
		3 mmol		Nil	100	Nil
5	Compound V	1 mmol	0.12	0.07	41.6	0.39
		2 mmol		0.06	50	0.34
		3 mmol		0.05	58.3	0.28
6	Compound VI	1 mmol	0.10	0.04	60	0.22
		2 mmol		0.03	70	0.17
		3 mmol		0.02	80	0.11

The corrosion rate decreases as increase the inhibitors concentration. All tested compounds showed corrosion inhibition in 1 M HCl due to their larger molecular size that facilitates better surface coverage. The corrosion inhibition efficiency of the complexes decreased in the following order

Compound IV > compound III > compound VI > compound II > compound I > compound V

In literature the inhibition efficiency of hetero atoms sequence given as follows O < N < S < P [11]. Because of this reason compound IV contains more number of electron donor hetero atoms O, N, S and P exhibited better inhibition effect compared to other compounds.

Adsorption isotherm

The inhibitors decreased the corrosion rate and blocking the corrosion sites by adsorption. Among the several adsorption isotherms the degree of surface coverage (θ) at different concentrations of the inhibitors were used to determine the best isotherm for the adsorption process. The experimental data gave a straight line graph when plotted of C/θ versus C which is fitted with Langmuir adsorption isotherm. This is illustrated in **Figure 2.**

$$\frac{C}{\theta} = \frac{1}{k} + C \quad (3)$$

C – Concentration of the corrosion inhibitor
θ – Degree of surface coverage
K – Adsorption equilibrium constant

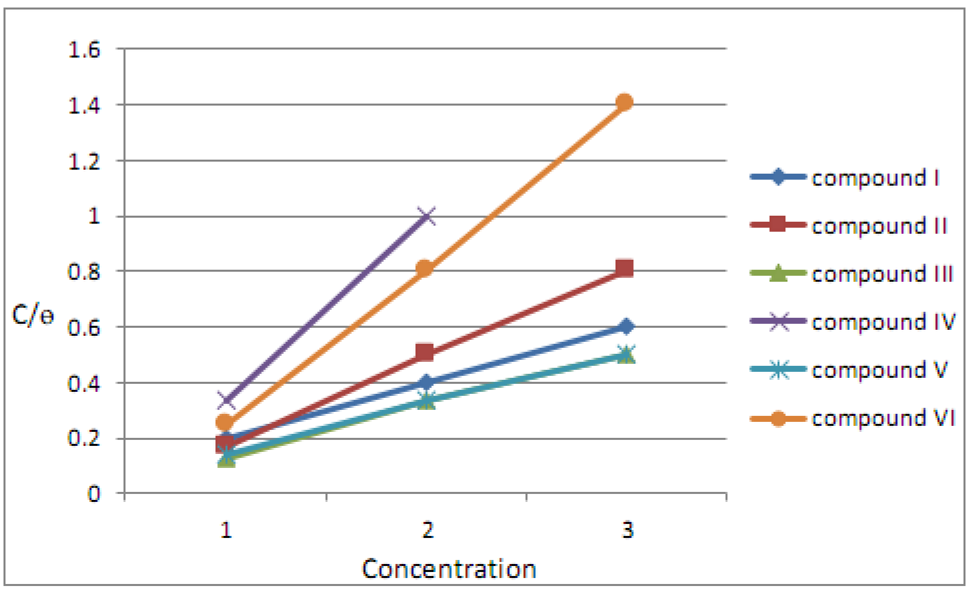


Figure 2: Langmuir's adsorption isotherm for mild steel in 1 M HCl in presence of inhibitors at different concentrations

It was assumed that the inhibitors molecules formed monolayer adsorption on the metal surface follow the Langmuir's adsorption isotherm.

Conclusions

Copper(II) amino acid complexes were synthesized and their inhibition of mild steel corrosion was studied using weight loss method. All the synthesized copper(II)aminoacid complexes inhibited corrosion of mild steel in 1M HCl. Among them [CuCl(SCys)PPh_3H_2O] complex possesses excellent inhibition efficiency at 3 mmol concentration. The rate of corrosion decreases and the corrosion inhibition efficiency increases by increasing the inhibitor concentration. The inhibition process obeyed the Langmuir adsorption isotherm.

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